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**Selenium in Kesterson Reservoir Ephemeral Pools Formed
by Groundwater Rise: I. A Field Study**

Tetsu K. Tokunaga and Sally M. Benson

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ABSTRACT

One of the principal initial plans for managing Se contamination at Kesterson Reservoir (Merced County, California) entailed excavation to a depth of at least 0.15 m in order to remove soils with Se concentrations higher than 4 mg kg^{-1} . Prior to implementing this plan, surface waters were collected from numerous shallow ephemeral pools that formed during the winters of 1986 to 1988. Elevated concentrations of Se were measured in all of these pools. Pools formed during this period from a combination of overland flow from adjacent non-seleniferous pond waters, rainfall ponding, and emergence of the fluctuating shallow water table above the soil surface. Selenium in these ephemeral pool waters originated primarily from dissolution of surface salt crusts and from displacement of seleniferous soil solutions up to the surface. Through the monitoring of a test plot where 0.30 m of the surface soil had been removed, the potential was demonstrated for shallow water table rise to displace seleniferous soil solutions to the surface, resulting in highly seleniferous ephemeral pools. In the test plot, ephemeral pool Se concentrations often exceeded $10^3 \mu\text{g L}^{-1}$. This study clearly demonstrated (i) that pools formed over soils with total Se concentrations in the range of 0.5 to 1.7 mg kg^{-1} could still provide a highly seleniferous aquatic environment, (ii) that the total Se concentration in a soil can be a misleading parameter to use in determining target goals for remediation, and (iii) that the excavation strategy was inappropriate for the Kesterson Reservoir setting.

great variability exists, the average total Se concentration in the surface 0.15 m of soil was about 5 mg kg^{-1} . Below depths of about 0.15 m, the total Se concentrations were generally less than 2 mg kg^{-1} . The explanation for this partitioning of Se was provided by Weres et al. (1899b). During ponding with drain waters, the pond bottoms provided generally anaerobic conditions through which the percolating waters passed. The Se in drain and pond waters was dissolved primarily as selenate [Se(VI) as SeO_4^{2-}]. Upon entering the anoxic pond bottoms, microbially mediated reduction of Se(VI) occurred (e.g., Oremland et al., 1989). Products of reduction included selenite [Se(IV) , as HSeO_3^- and SeO_3^{2-}], elemental Se, and various forms of organic Se. Selenite, although moderately soluble in these waters, is strongly adsorbed in neutral to slightly alkaline soils (e.g., Geering et al., 1968; Elrashidi et al., 1987; Neal et al., 1987). Elemental Se is practically insoluble. Organic Se generally comprised less than 1% of the dissolved Se inventory (Long et al., 1990). Thus, during ponding, Se in the infiltrating waters was selectively immobilized within the surface soils. However, reductive immobilization of Se within the surface 0.15 m of soils has not been

KESTERSON RESERVOIR, at the northern terminus of the San Luis Drain, is situated in the San Joaquin Valley, 20 km north of Los Banos, California. The 520-ha system of ponds was located in the southern portion of the Kesterson National Wildlife Refuge (2390 ha). The Reservoir was comprised of a set of 12 shallow evaporation ponds used for the disposal of agricultural drainage waters (Fig. 1). Drainage water was supplied via the San Luis Drain, which extended 137 km to the south, into the source area of the southwestern San Joaquin Valley. Kesterson Reservoir had been used for disposal of drainage water from irrigated agricultural fields from 1981 to 1986. Along with high salinity ($\text{EC} \approx 1.5 \text{ S m}^{-1}$), this drain water was found to be concentrated with respect to a number of trace elements. The correlation between elevated concentrations of Se in ponded drain waters and reproductive failures of nesting waterfowl at Kesterson Reservoir was established in 1983 (Ohlendorf, 1989). As a result, discharge of seleniferous drain waters into the Reservoir was terminated in 1986.

Despite the termination of inputs of drain waters, a substantial residual inventory of Se, other trace elements, and salts was left in the previously ponded soils. Selenium in particular accumulated largely within the surface 0.15 m of the soil profiles, and commonly was not leached in high concentrations into deeper regions of the soil profile or shallow aquifer. While

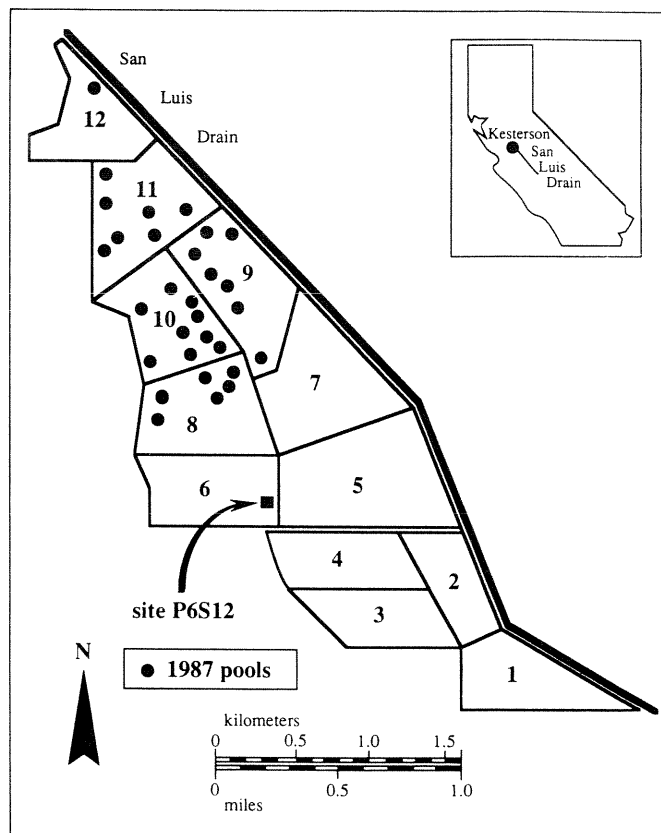


Fig. 1. Map of Kesterson Reservoir, showing locations of some of the sampled 1987 ephemeral pools and the excavated study site P6S12.

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completely effective. Approximately 20% of the total Se inventory at Kesterson Reservoir is distributed below 0.15 m, generally within 1.0 m of the soil surface. While this represents a minor fraction of the total Se inventory, a considerable portion of this deeper inventory resides in the mobile soil solution (Weres et al., 198b; Long et al., 1990; Tokunaga et al., 1991). Furthermore, throughout much of the upper 1 m of soils, the Se concentrations in soil solutions range from 10^2 to 10^4 $\mu\text{g L}^{-1}$, with characteristic concentrations of about 10^3 $\mu\text{g L}^{-1}$. The present surface water quality goals for wildlife habitat range from 2 to 5 $\mu\text{g Se L}^{-1}$.

Information concerning the behavior of the Se inventory in surface soils subjected alternately to flooding and drying conditions is also available. Upon reexposure to aerated conditions with the cessation of pond operations, the previously insoluble and adsorbed Se inventories of the surface soils are susceptible to reoxidation. While the kinetics of reoxidation in Kesterson soils remain to be studied, some practical implications of this process have been observed in the field (e.g., Long et al., 1990). Reoxidation leads to a return of some fraction of the previously immobilized Se to the soil solution. The Se in solution, primarily as SeO_4^{2-} , is free to be transported within the soil profile and in the food chain. Selenate transport is of potential concern in the formation of ephemeral pools, and in leaching into the shallow groundwater.

In some nonponded areas of Kesterson Reservoir, the shallow, fluctuating water table contributed to the annual formation of ephemeral pools (Fig. 1). The local shallow water table rises rapidly during October and November, primarily in response to the annual flooding of adjacent private duck clubs and wildlife refuges. The annual maximum water table height occurs during the months of January through March.

After termination of drain water disposal at Kesterson Reservoir, one of the site management options given serious consideration entailed excavation of the surface soils to depths of 0.15 m or more in many of the former ponds. A total Se concentration of 4 mg kg^{-1} or less within the surface 0.15 m of soil was selected as the cleanup goal (U.S. Bureau of Reclamation, 1986). Areas with Se concentrations in excess of this goal were to be excavated. Such an excavation program would have removed over 70% of the Se inventory from the former pond sediments. The excavated soils were to be contained indefinitely in a lined landfill located at Kesterson Reservoir, and hence this strategy was referred to as the Onsite Disposal Plan (ODP). With the termination of all controlled inflows of water into the former ponds, advocates of the ODP expected the site to revert to a clean habitat.

In view of previously noted depth distributions of soluble Se within the affected soil profiles and the yearly rise of the shallow water table, it was anticipated that problems of seleniferous ephemeral pool formation would arise annually in excavated areas. In particular, implementation of the ODP was expected to result in an increased probability of seleniferous ephemeral pool formation that in turn could result in increased waterfowl exposure to Se. The mechanism of upwards displacement of seleniferous soil waters by the yearly rise of the shallow water table was ex-

pected to result in pools of both high Se concentration and high salinity. As the water table annually rose through the Se-enriched soil, it incorporated increasing amounts of salts and soluble Se that were present in the vadose zone. Where this Se and salt-enriched water table rose above the soil surface, the resulting ephemeral pools were expected to contain elevated concentrations of soluble Se. Rainfall dilution can provide a moderating effect, but is unreliable in this semiarid region (mean annual precipitation ≈ 300 mm). Furthermore, the excavation would in itself clearly lower the residual soil surface, leaving larger areas of the site susceptible to pool formation.

This paper presents results of monitoring soluble Se and salt distributions within a soil profile in an excavated test plot (simulating ODP conditions), along with ephemeral pool water quality data from this and other locations within Kesterson Reservoir. Only the period from 1987 to late 1988 will be addressed in detail. More recent field observations will be briefly noted. In an accompanying paper (Poister and Tokunaga, 1992), laboratory experiments on Kesterson Reservoir ephemeral pool formation are presented.

MATERIALS AND METHODS

Numerous ephemeral pools had been observed at Kesterson Reservoir during the months of November through May 1987. Pool water samples were periodically collected using a syringe, filtered (0.45 μm), and analyzed for various solutes. Only the Se and salinity data will be presented in this paper. Selenium analyses of these surface waters, as well as of soil solution samples and water-extracts of soils were performed by hydride generation atomic absorption spectrometry (HGAAS) as described by Weres et al. (1989a).

The field test plot at which the majority of ephemeral pool monitoring was conducted is located 33 m west of the eastern boundary of Pond 6, and is referred to as Site P6S12 (Fig. 1). The site is mapped under the Turlock series (Albic Natraqualf) in a recent (draft) soil survey. In an earlier study (Cole et al., 1952) the site, as well as most of the present Kesterson Reservoir area, has been mapped under the Waukena series. These soils were recognized as being saline, and in some cases saline-sodic, in this earlier survey. The P6S12 site was developed (excavated and instrumented) in order to monitor potential consequences of the ODP. The site was originally vegetated with cattails (*Typha* sp.), and was subject to periodic flooding with seleniferous drain waters during the operation of Kesterson Reservoir. The last extensive period of flooding at this site probably occurred in early 1986. The site may have experienced minor periods of ponding as recently as March 1987. The adjacent Pond 5 (Fig. 1) was continuously flooded with nonseleniferous waters during the period of investigation addressed in this present paper. (Ponds 1, 2, and 7 were also flooded with nonseleniferous waters during this period.)

The test plot was prepared by excavating the surface soil to a depth of 0.30 ± 0.10 m below the original cattail rhizome-soil interface. The nominally square plot, with an approximate area of 65 m^2 , was excavated in May 1987 at the end of the 1986–1987 wet season. Analyses of five residual soil surface samples (0.15-m deep cores) indicated that the total Se concentrations were in the range of 0.5 to 1.7 ± 0.5 mg kg^{-1} , i.e., well below the targeted soil cleanup goal. Total Se analyses were performed by x-ray fluorescence spectrometry (Giauque et al., 19786). The test plot was monitored with soil water samplers, tensiometers, and a piezometer. Tensiometers were initially installed at depths of 0.15, 0.30, 0.46 and 0.61 m. After the 1st yr,

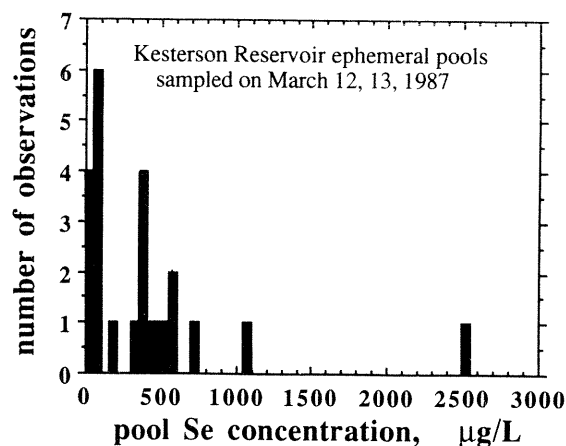
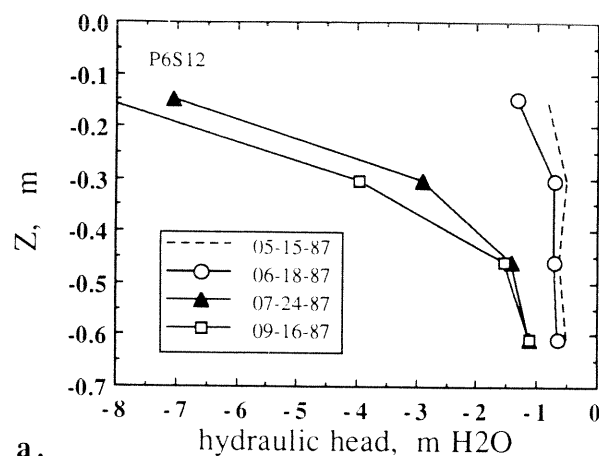


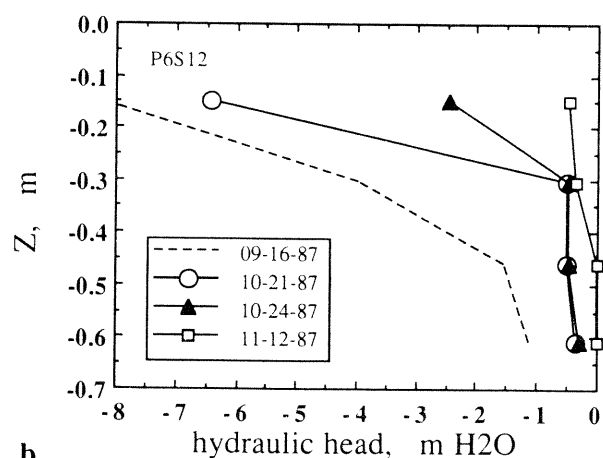
Fig. 2. Histogram of Se concentrations in ephemeral pools sampled in March 1987. The minimum, geometric mean and maximum Se concentrations were 38, 197, and 2550 $\mu\text{g L}^{-1}$, respectively.

additional tensiometers at 0.08-, 0.76-, and 0.91-m depths were installed along with a second set of 0.15- and 0.30-m tensiometers. The piezometer permitted measurements of depths to groundwater down to 2.03 m below the residual soil surface. Soil water samplers were installed at depths of 0.15, 0.30, 0.46, 0.61, 0.91, 1.07 and 1.22 m. During the 1987–1988 and 1988–1989 wet seasons, the soil water samples were equipped with extension tubing (3.2-mm i.d., 6.4-mm o.d. polyethylene) for remotely collecting soil solutions. This modification permitted sampling of soil solution profiles from a point outside the boundary of the plot, thus avoiding excessive disturbance of the test plot soil surface. At three locations in the test plot, cylindrical rings, 0.29, 0.33 and 0.56 m in diameter, were partially embedded into the residual soil surface (with the ring axes oriented vertically). Ponded waters collected from within the rings were effectively isolated from possible lateral contamination from the plot boundaries. Differences in ponded water elevations between the interior and exterior of individual rings were commonly observed. Such differences indicated that leakage along the walls of the rings was minor, and that isolation from possible lateral contamination was in fact achieved. Surface waters were collected with a syringe and passed through 0.45- μm filters.

Changes in the water-soluble Se and soluble salts inventories within the upper 0.15 m of the residual soil surface were monitored through periodic core sampling at 60- to 180-d intervals. The 0.15 m long, 0.050-m diam. cores were obtained from five sampling areas within the test plot during each sampling event. Wood or plastic pegs were driven into the surface holes resulting from core sampling to prevent future coring of previous sampling points, and to minimize mixing of the surface soils from the caving of holes. Soil samples were homogenized at field-moisture contents and passed through a 4.75-mm sieve. The common practice of air drying samples prior to extraction was not employed in order to minimize possible accelerated oxidation of Se during sample processing. Water-extractable Se contents of the soil cores were obtained by mixing 30 g soil samples with distilled water in 1:5 (kg kg^{-1}) mass ratios for 1 h. Water-extractable Se concentrations obtained by either mixing with a magnetic stirrer or on a reciprocating shaker have been found to be equivalent and have been used interchangeably. The mixtures were centrifuged (1000 RCF, 10 min) and the supernatant solutions filtered (0.45 μm) prior to analyses. Water-extract solutions were analyzed for Se by HGAAS as noted earlier. Along with Se analyses, the electrical conductivity (EC) of the extracted solutions was also measured.



a.



b.

Fig. 3. (a) Hydraulic head profiles at site P6S12 during the 1987 drying cycle. The gravitational potential datum is taken at the residual soil surface. (b) Hydraulic head profiles at the site during the 1987 rewetting cycle. Note that the hydraulic head data indicate that rewetting resulted primarily from water table rise.

RESULTS AND DISCUSSION

Ephemeral pool formation at Kesterson Reservoir during the 1986–1987 and 1987–1988 wet seasons was a result of overland flow from adjacent flooded ponds, the surfacing of the rising shallow water table and rainfall ponding. The relative importance of each of these factors varied among different pools, and also through time within individual pools. The more persistent pools were usually associated with lower elevations, and often with overland flow from adjacent ponds. Locations of some of the March 1987 ephemeral pools sampled after a 55-mm rainfall event (with 117 mm of prior rainfall during the 1986–1987 wet season) are indicated in Fig. 1. Selenium concentrations in these March 1987 ephemeral pools are summarized in the Fig. 2 histogram. The geometric mean of the Se concentrations in Fig. 2 was 197 $\mu\text{g L}^{-1}$. Even the lowest Se concentration of 38 $\mu\text{g L}^{-1}$ in this sampling greatly exceeded the 2 to 5 $\mu\text{g L}^{-1}$ goal for surface water habitats.

During the period from May 1987 to September 1987, the P6S12 soil experienced drying resulting from both water table decline and evaporation. The latter

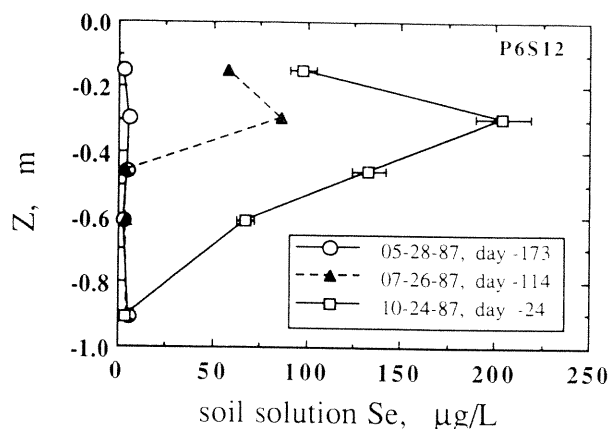


Fig. 4. Soil solution Se concentration profiles during the 1987 drying cycle at the P6S12 study site. Samples were collected in vacuum soil solution samplers.

process was clearly indicated in tensiometer measurements (Fig. 3a). At its lowest stage during September, the water table was about 1.0 m below the residual soil surface. From September 1987 through November 1987, the soil profile was resaturated largely through water table rise as indicated by the tensiometer data (Fig. 3b). In these data, rewetting of the soil profile (indicated by increases in hydraulic head), progresses from the lower region of the profile upwards. Only 33 mm of rainfall occurred during this stage of rewetting. By 17 Nov 1987, the first appearance of surface water at this site was observed and sampled. Ponding depths at this site continued to increase until late January 1988, when maximum depths were measured, ranging from 0.10 m to 0.25 m at various locations.

Depth profiles and time trends of soil solution Se concentrations obtained from field soil water samples during the 1987 drying cycle are shown in Fig. 4. Selenium concentrations in the soil profile were uniformly low ($\leq 7 \mu\text{g L}^{-1}$) during the initial stages of the study (May 1987). As noted earlier, commonly less than 20% of the total Se in these soils occurs in immediately water-soluble forms. The increases in soil solution Se concentrations through October 1987 are probably a result of oxidation of various Se species to Se(VI). Increases in the soil profile soluble Se inventory can not be explained by inflow from greater depths because of the generally much lower soluble Se concentrations associated with deeper strata at this site. Similar time trends over longer periods have been observed in other soils at Kesterson Reservoir after cessation of ponding (Tokunaga et al., 1991).

Water-extracted Se concentrations from surface soil core samples collected in the residual soil are presented in Fig. 5. In this figure, the data points prior to the emergence of the water table span a similar period of time as that covered in the soil profile data of Fig. 4. During this period, an increase in the soluble Se fraction is also apparent from the Se removed with water extracts of the residual surface soil (0–0.15 m) shown in Fig. 5. In this figure, the water-extracted Se has been normalized to an equivalent concentration in a soil solution at a soil water content of 0.30 kg kg^{-1} . (Water-saturated soils from the test plot have soil water contents of approximately 0.30 kg kg^{-1} .)

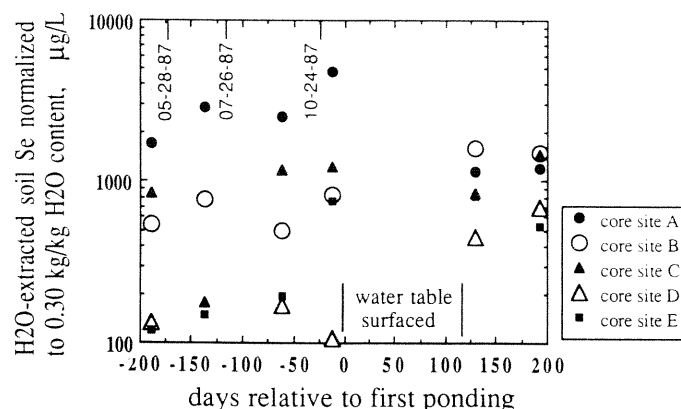


Fig. 5. Soluble Se in the residual soil surface, 0 to 0.15 m, of the P6S12 study site. Time zero, the date of first emergence of the water table, was 17 Nov. 1987. Data were obtained from 1:5 soil/water extracts, with Se concentrations normalized back to soil solution concentrations at gravimetric soil water contents of 0.30 kg kg^{-1} . See text for details.

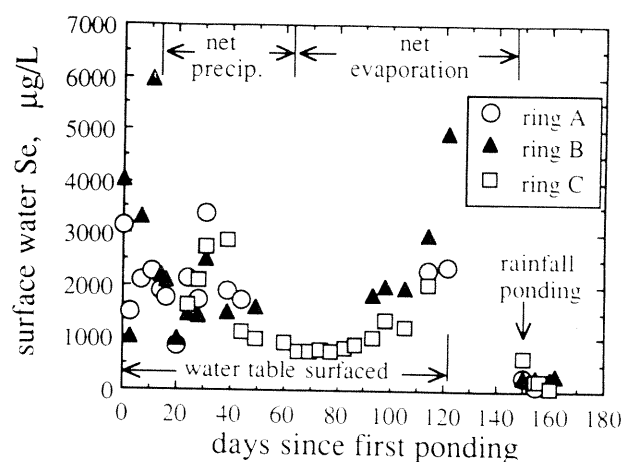


Fig. 6. Se concentrations measured in ephemeral pools on the P6S12 study site during the 1987–1988 wet season. Time zero refers to the first emergence of the water table on 17 Nov. 1987.

The normalization of water-extracted Se concentrations to this soil water content was done in order to estimate soil Se concentrations under conditions where the soil has become essentially water saturated, and will assist in later comparisons between water-extracted Se inventories and Se concentrations in the 1987–1988 ephemeral pond waters at the site. Considerable spatial variability of water-extracted Se is also evident from this data. Nevertheless, it is clear that very high concentrations of water-soluble Se can occur in pond waters over soils that are well below the initially selected 4 mg kg^{-1} total soil Se cleanup goal.

As noted previously, the shallow water table emerged above the residual soil surface, resulting in ephemeral pool formation in November 1987, reached a maximum in late January 1988, then receded below the surface in late March 1988. Surface water samples were collected from inside the sampling rings throughout this period. Selenium concentrations from various samplings are depicted in Fig. 6. Ponded waters with Se concentrations in excess of $10^3 \mu\text{g L}^{-1}$ were com-

monly obtained. The initially very high Se concentrations are within the range of expected values based upon water extracts of the residual soil surface. The decline in surface water Se concentrations with time is a result of further upwelling of less seleniferous soil waters, dilution resulting from rainfall, and perhaps Se(VI) reduction and algal uptake. These concentrations of Se typically exceeded the original drain water Se concentrations by at least fourfold. Comparison of Fig. 5 and 6, where Se concentrations are on the order of $10^3 \mu\text{g L}^{-1}$ in both data sets, suggests that the surface soil soluble Se inventory served as a fairly reliable predictor for ephemeral pool Se concentrations resulting during the 1987–1988 water table rise. The increase in Se concentrations in March 1988 (Day 105–122), during which only 3 mm of rainfall occurred, appear to have resulted from evaporative concentration. Pond salinity trends during this period support this explanation.

The salinity of the pond waters, as inferred from electrical conductivity (EC) data (Fig. 7), approximately paralleled the trends in pool water Se concentrations during the period in which the shallow water table remained emerged. The roughly parabolic trends in both surface water Se concentrations (Fig. 6) and EC's (Fig. 7) probably reflect initially highly concentrated solutions characteristic of the surface soils, which became more dilute as less concentrated soil solutions emerge and while rainfall exceeded pan evaporation. The dilution stage was followed by a reconcentration period dominated by evaporation and recession of the water table. Rainfall exceeded pan evaporation during the period spanning 1 Dec. 1987 through 20 Jan. 1988 (Day 14–64 relative to the initial emergence of the water table). Pan evaporation exceeded rainfall during the period of 21 Jan. 1988 through 13 Apr. 1988 (Day 65–148). Note that ponding of the shallow water table ended on around 22 Mar. 1988 (Day 126). The increases in surface water Se concentrations and EC's measured between Day 65 and 121 are generally consistent with evaporative concentration.

After the decline of the water table below the residual soil surface, additional ponding occurred in late

April 1988 as a result of rainfall (45 mm). The April 1988 rainfall ponding (Day 150–162) differed from previous conditions since the surface water composition was determined by mixing and dissolution of salts (including Se) in rain water, rather than by displacement of the near surface soil solution. Although the salinities of these pools were within the range of values measured during emergence of the shallow water table, 1.8 to 6.2 S m^{-1} , Se concentrations were considerably diminished. This relative decline in redissolved Se is possibly a result of partial reduction of Se(VI) to Se(IV) in the soil surface. Nevertheless, the Se concentrations on the order of $10^2 \mu\text{g L}^{-1}$ are considerably higher than the surface water quality goal. It should be noted that ephemeral pools formed primarily from rainfall ponding at Kesterson Reservoir (1987–1990) have generally been both less saline and less seleniferous than the surface waters of rainfall origin sampled in the test plot during April 1988.

During the 1988–1989, 1989–1990, and 1990–1991 wet seasons, the maximum height of the water table has remained deeper than 0.40 m below the residual soil surface. The discontinuation of flooding in the adjacent Pond 5 in May 1988 accounted for most of the lowering of the more recent water table maxima. Since discontinuation of intentional flooding at Kesterson Reservoir, the dominant influence on local water table fluctuations has been the annual flooding and draining of the surrounding seasonal wetlands. Year to year variations in water deliveries to these wetlands along with variations in rainfall patterns appear to account for most of the observed fluctuations in the elevation of the water table at Kesterson Reservoir. The water table is expected to rise above the ground surface at the P6S12 site and other areas of low elevation at Kesterson Reservoir when rainfall is 50% higher than average. However, the primary mechanism for pool formation will be ponding of rainfall.

SUMMARY

The results of this work show the displacement of Se and salts upwards by the rise of a shallow water table, and the subsequent ponding of these waters in an excavated plot. Selenium concentrations in the test plot generally exceeded surface water quality goals by at least two orders of magnitude. It has been demonstrated that in the Kesterson Reservoir environment, the proposed remediation strategy involving excavation of the soil surface (ODP) would potentially be counterproductive with respect to preventing future occurrences of ponding with seleniferous waters. Excavation would enlarge the areal extent of seasonal ponding. The soluble Se inventory at depth is sufficiently large so that upward displacement of the soil solution by the annual rise of the water table could result in the accumulation of highly seleniferous surface waters in topographically lower portions of Kesterson Reservoir. Deeper excavations would clearly result in higher probabilities of pool formation resulting from water table rise, and also enhance evaporative accumulation of salts (including Se).

The results of this study assisted in the rejection of the ODP approach to managing Kesterson Reservoir. The concern over future pool formation as a result of

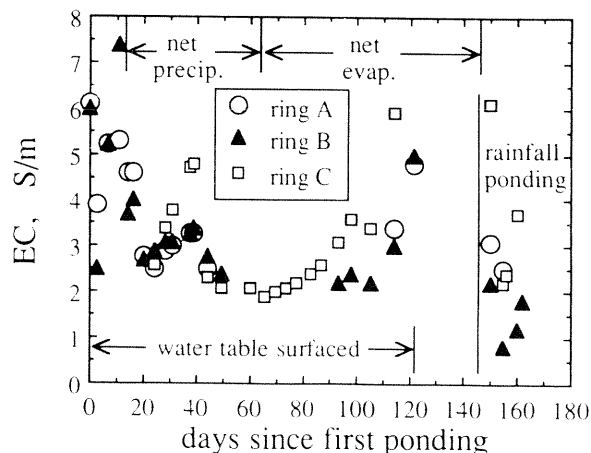


Fig. 7. Electrical conductivities of ephemeral pool waters in the P6S12 study site during the 1987–1988 wet season. Time zero refers to the first emergence of the water table on 17 Nov. 1987.

shallow water table emergence motivated the California State Water Resources Board to order the U.S. Bureau of Reclamations to fill most of the topographically low areas at Kesterson Reservoir with additional soil. Filling was completed in October 1988. Both the filled and unfilled regions have become upland habitat. During the past several years, enhanced dissipation of Se by microbial volatilization (Frankenberger and Karlson, 1989) has been investigated, and is currently being considered for full-scale implementation. Possible future appearance of Se in surface waters via diffusion and upward flow into the surface fill soil, followed by mixing in ponded rain waters is currently recognized as an ongoing concern in the management of Kesterson Reservoir. Provisions for surface drainage in order to prevent future ponding during wetter than average years are currently being evaluated.

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